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Muff, Jens; Bennedsen, Lars Rønn; Søgaard, Erik Gydesen

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Department of Biotechnology, Chemistry, and Environmental Engineering
Aalborg University

Detailed Parameter Study on the Mechanisms in Electrochemical Oxidation of p-Nitrosodimethylaniline in Chloride Electrolyte

Muff J.*, Bennedsen L.R. & Søgaard E.G.

Abstract
p-nitrosodimethylaniline (RNO) has been widely applied as a selective probe compound for OH· detection in electrochemical oxidation studies. However, the present study showed that RNO was oxidised by chemisorbed active oxygen (MO) at the surface of a Ti/Pt_{90}-Ir_{10} anode and by free chlorine species as well with no interaction from intermediate OH· groups. Hence, RNO can not be regarded as a OH· selective probe compound, but is still a useful method for overall evaluation of oxidation performance.

1. Introduction

Determination and quantification of hydroxyl radicals is a challenging task due to its extremely reactive nature, existing only in the order of nanoseconds. When produced in relatively high concentrations, direct detection by electron spin resonance (ESR) is possible, but for detection of low concentrations of hydroxyl radicals, indirect techniques apply involving trapping of the hydroxyl radical by an addition reaction (spin trap) to produce a more stable radical (spin adduct) [1]. p-nitrosodimethylaniline (RNO) is a widely applied spin trap compound in several fields of chemistry and is reported to be very selective to hydroxyl radicals.

During the last 15 years, electrochemical oxidation has been developed into a strong physico-chemical oxidation technique for degradation of organics in polluted water utilizing hydroxyl radicals and lattice active oxygen depending on the electrode material used [2]. In electrochemical oxidation studies, bleaching of the organic dye molecule RNO has been used as a tool for evaluation of the oxidative performance. RNO is claimed to act as a selective probe compound towards hydroxyl radicals through a one electron oxidation of the chromophore nitroso group (fig. 1).

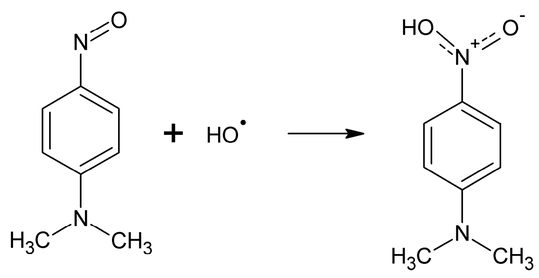

Figure 1: Oxidation of RNO
The one electron oxidation of the nitroso group in p-nitrosodimethylaniline (RNO) by the hydroxyl radical, which bleaches the yellow colour.

However, discrepancies were found in literature regarding RNO being bleached by other oxidative species; even though RNO was showed to be electrochemically inactive at Pt, IrO_2, SnO_2 and PbO_2 anodes by cyclic voltammetry [1,3], bleaching and hence oxidation was observed in Ti/Pt and Ti/RuO_2 anode systems [4], types of anodes, which according to the generally accepted models [1,2,5], utilize chemisorbed lattice active oxygen, MO or MO_{x+1}, due to a higher adsorption enthalpy towards the adsorbed hydroxyl radical [2]. In addition, several studies report bleaching of RNO by other strong oxidants as ozone [9] and chlorine [4,6]. The bleaching by these oxidants was explained by oxidation mechanisms through radical chain reactions generating hydroxyl radicals as the main intermediate oxidative agent [7-9].

2. Aims of the study

- Question the role of RNO as a fully selective hydroxyl radical probe compound
- Determine the kinetics of RNO bleaching in different electrolyte systems; direct vs. indirect oxidation
- Investigate the ability of chlorine oxidation of RNO in chloride mediated electrochemical oxidation at different pH
- Investigate the proposed role of hydroxyl radicals in chlorine oxidation
- Compare the bleaching power of chloride mediated oxidation and added alkaline sodium hypochlorite solution,

3. Materials and Methods

The Ti/Pt_{90}-Ir_{10} anode material was specifically chosen for this study for two reasons; its high efficiency towards chloride oxidation, and to investigate if RNO was oxidised by chemisorbed active oxygen.

The experimental setup is seen in figure 2 and the applied cell configuration and settings are seen in table 1 and table 2.

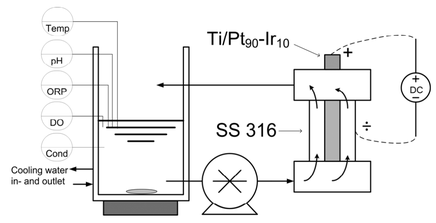

Figure 2: Experimental setup
Batch recirculation of the RNO solution from a water cooled reservoir through the EC cell of tubular design.

Table 1: Cell configuration and experimental settings	
Type of cell	Tubular, single compartment
Anode	Ti/Pt_{90}-Ir_{10}
Cathode	SS 316
Anode surface area	60.3 cm^2
Electrode gap	6 mm
Cell volume	43 ml
Mass transfer coeff.	$2.25 \cdot 10^{-5}$ m s^{-1}
Experimental mode	Batch recirculation
Flow rate	430 L h^{-1}
Total volume	3 L
Current density	32 mA cm^{-2}
Initial RNO conc.	10 mg L^{-1} ($6.66 \cdot 10^{-5}$ M)
Electrolytes	Na_2SO_4, $NaNO_3$, Na_2HPO_4, NaH_2PO_4, Na_3PO_4, and NaCl
Concentration range	0.001 – 0.154 M
pH range	6-11
OH· scavenger	Tertiary butyl alcohol (t-BuOH)
Temperature	20±1 °C

Table 2: Settings of chemical bleaching experiment	
Oxidant	Alkaline NaOCl solution
Concentration	0.272 M
Flow rate	1.18 mL min^{-1}

The bleaching of RNO was followed by UV/VIS spectroscopy at 440 nm with a linear calibration curve in the applied concentration range. The absorbance decreased dramatically under acidic conditions, but remained constant in the neutral and alkaline pH range (fig. 3).

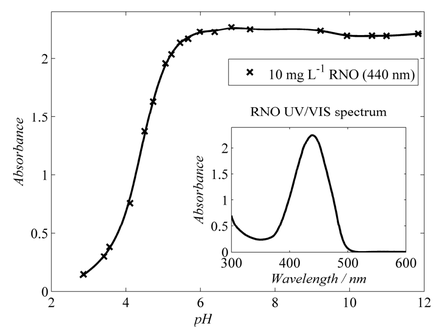

Figure 3: RNO absorbance vs. pH
The absorbance of RNO remained constant in the neutral and alkaline pH range, but decreased under acidic conditions. Subplot: UV/VIS spectrum (pH=7.3), $\lambda_{max.\ abs.}$ = 440 nm.

4. Results and Discussion

Experiment 1 (pure electrolytes)

Main results (fig. 4a, b and c):
- RNO was directly oxidized in Na_2SO_4 at the anode surface
- The rate of oxidation was increased in Na_3PO_4 and $NaNO_3$
- The direct oxidation followed 1. order reaction kinetics ($k = 9.67 \cdot 10^{-5} – 1.35 \cdot 10^{-4}$ s^{-1})
- The rate of oxidation was highly increased in NaCl due to indirect free chlorine oxidation
- The indirect oxidation followed 2. order kinetics with respect to RNO ($k = 1.17 \cdot 10^{-5}$ M^{-1} s^{-1})

Lessons learned:
- RNO was oxidized by chemisorbed, MO, active oxygen

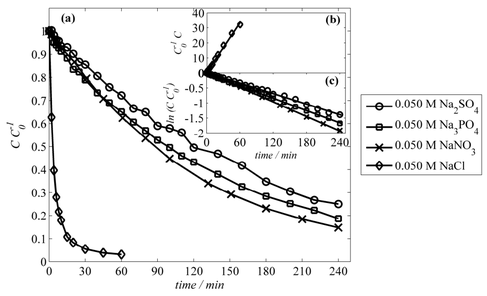

Figure 4: EC oxidation in pure electrolytes
RNO was bleached by direct oxidation in Na_2SO_4, Na_3PO_4, and $NaNO_3$. The oxidation was greatly enhanced by chloride mediated indirect oxidation by free chlorine species in NaCl.

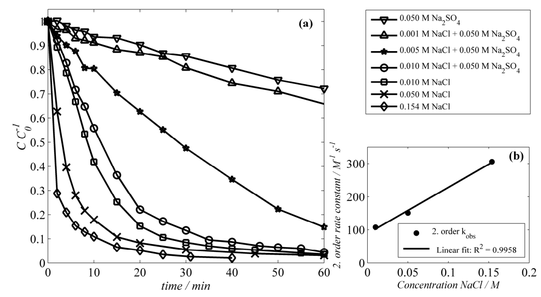

Figure 5: EC oxidation in mixed and NaCl electrolytes
Increased chloride concentrations shifted reaction kinetics from 1. to 2. order RNO dependence. In pure NaCl, the apparent rate constant, k_{obs}, was linear correlated with [Cl^-].

- RNO was chemically oxidized by free chlorine species
- Different oxidation mechanisms applied for direct and indirect oxidation of RNO

Experiment 2 (mixed and NaCl electrolytes)

Main results (fig. 5a and b):
- Addition of 0.001 and 0.005 M NaCl to a 0.050 M Na_2SO_4 supporting electrolyte significantly enhanced the rate of oxidation
- Higher NaCl concentrations turned the reaction kinetics from 1. to 2. order as expected
- In pure NaCl electrolyte, 2. order rate constants were linear correlated to NaCl concentration

Lessons learned:
- High cell voltage (17.8 V) compared to low (4.9 V) slightly increased oxidation rate at galvanostatic conditions
- Further indications were found for the indirect chloride mediated oxidation of RNO

Experiment 3 (NaOCl vs. in-situ free chlorine)

Main results (fig. 6):
- RNO was chemically oxidized by physically added alkaline NaOCl solution
- The rate of the simulated chemical chlorine oxidation was much slower compared to the rate of oxidation by in-situ generated free chlorine

Lessons learned:
- The oxidation power of in-situ generated free chlorine is superior to common chlorination
- May be due to chloride/chlorine being adsorbed to the anode surface during the electrolytic formation as proposed by Bonfatti et al. [5]. In this way RNO was both directly oxidized by chlorine upon contact with the anode surface and indirectly through mediated bulk oxidation resulting in higher oxidation efficiency.

Experiment 4 (role of OH·)

Main results (fig. 7):
- Similar oxidation rate was found with or without the presence of 0.05 M t-BuOH in a 0.050 M Na_2SO_4 electrolyte
- Neither 0.05 M nor 0.10 M t-BuOH slowed or even affected the rate of RNO oxidation in the 0.050 M NaCl electrolyte
- Addition of 0.015 M of the reducing agent $Na_2S_2O_3$ to the 0.050 M NaCl electrolyte hindered the initial RNO oxidation due to chlorine neutralization. The oxidation continued when $S_2O_3^{2-}$ was depleted

Lessons learned:
- No hydroxyl radicals was formed by the Ti/Pt_{90}-Ir_{10} anode material
- The hydroxyl radical chain reaction proposal was rejected and the indirect RNO oxidation by chlorine was entirely due to the oxidative abilities of the hypochlorous acid/hypochlorite pair.

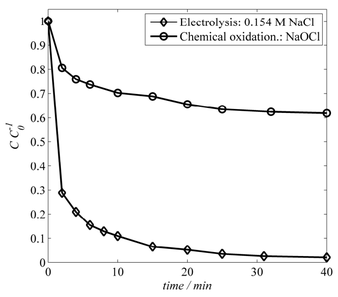

Figure 6: NaOCl vs. EC in-situ free chlorine
NaOCl was added to the RNO solution in a flow rate and concentration comparable to the chlorine production rate by electrolysis in a 0.154 M NaCl electrolyte.

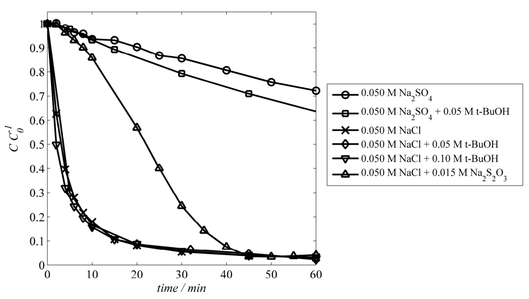

Figure 7: Study on the role of hydroxyl radicals
Tertiary butyl alcohol as OH· scavenger had no influence on neither the direct nor the indirect oxidation performance.

5. Conclusions

- RNO can not be regarded as a fully selective hydroxyl radical probe compound in electrochemical oxidation studies, since:
  - RNO was directly oxidized by chemisorbed oxygen, MO, at Ti/Pt_{90}-Ir_{10}
  - RNO was indirectly chemically oxidized by hypochlorous acid and hypochlorite
- No hydroxyl radicals were generated by Ti/Pt_{90}-Ir_{10}
- Hydroxyl radicals played no role as intermediate oxidant in free chlorine oxidation as formerly proposed [7-9]

However, RNO is still to be considered as a very applicable and easy to use compound for evaluation of the electrochemical oxidation performance, taking account of all oxidative species generated in the process.

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7. Contact information

*Corresponding author:

Jens Muff

Section for Chemical Engineering
Department of Biotechnology, Chemistry and Environmental Engineering
Campus of Esbjerg Institute of Technology
Aalborg University
Niels Bohrs Vej 8, DK-6700 Esbjerg, Denmark
(E-mail: *jm@bio.aau.dk*)

CIChem Colloid & Interface Chemistry group